

*Article*

## Apatite Formation on Rutile TiO<sub>2</sub> Film Deposited Using Dual Cathode DC Unbalanced Magnetron Sputtering

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**Abstract.** Rutile TiO<sub>2</sub> films were deposited on unheated stainless steel type 316L using dual cathode DC unbalanced magnetron sputtering. The effects of deposition time ranging 30, 60, 90, and 120 min on the films structure were investigated. Moreover, all the samples were immersed in SBF for period times of 3 and 5 days also considered. The crystal structures were characterized by thin film X-ray diffraction (TF-XRD). The film's thickness and surface morphology were evaluated using atomic force microscopy (AFM). The crystallinity, roughness, thickness, and grain size of rutile with only (110) plane increased with increased deposition time. After immersed samples in SBF for 3 day the highest and moderate crystallinity of apatite was observed on the 30 min and 90 min, respectively. However, the films deposited with 60 and 120 min cannot be observed the peak of apatite. An increase crystallinity of apatite clearly observed when after immersed in SBF for 5 day.

**Keywords:** TiO<sub>2</sub>, film, apatite, sputtering, deposition.

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## 1. Introduction

The titanium dioxide or titania ( $\text{TiO}_2$ ) is the ceramic material that exists in both crystalline and amorphous. Three crystalline polymorphs are anatase, rutile and brookite. Anatase and rutile have tetragonal structure, whereas brookite is orthorhombic in nature [1]. Both the anatase and rutile phases exhibit excellent biocompatibility properties on their surfaces through *in vivo* and *in vitro* studies [2]. However, the rutile phase is the most stable thermodynamically and has higher corrosion resistance than anatase [1]. Therefore, the rutile phase is suitable for biomaterials application. Normally, the rutile can be synthesized using thermal treatment of anatase phase at above  $600^\circ\text{C}$ , which causes some thermal stress inside. Recently, we reports that the rutile can be synthesized in low temperature using dual cathode DC unbalanced magnetron sputtering with various the external bias voltage to the substrates ( $V_{\text{sb}}$ ). The rutile plane (110) changed to (101) when the  $V_{\text{sb}}$  was increased to  $-150\text{V}$ . *In vitro*, the samples were immersed into the Kokubo's simulated body fluid (SBF) for 7 days. The denser and higher crystallinity of apatite was only observed on a sample synthesized with  $V_{\text{sb}}$  of  $-50\text{V}$ . Because, it exhibited the balanced properties of low surface energy of (110) rutile and close superposition of hydrogen-bonding group in (0001) apatite crystals on (101) rutile [3]. However, we do not report the influence of coating times on the  $\text{TiO}_2$  structures and formation of apatite.

In this work, rutile  $\text{TiO}_2$  films were deposited on unheated stainless steel type 316L substrate using dual cathode DC unbalanced magnetron sputtering with various deposition times ranging 30, 60, 90, and 120 min. *In vitro*, all samples were immersed in Kokubo's SBF [4] for period times of 3 and 5 days. The effects of deposition times on films structure and bioactive layer after immersion in SBF were investigated. A scanning electron microscope (SEM), atomic force microscopy (AFM) and thin film X-ray diffraction (TF-XRD) were used to analyze the rutile and bioactive layer.

## 2. Experimental

### 2.1. Sample preparation

Stainless steel type 316L (316L-SS) substrates were laser cutting in size of  $10\text{mm} \times 10\text{mm} \times 1\text{mm}$  (provided by Thainox Company, Thailand). All substrates were clean with ethanol, acetone, and DI-water ( $12.7\text{ M}\Omega$  electrical resistance) in ultrasonic for 5 min of each. The dual cathode DC unbalanced magnetron sputtering apparatus is a laboratory-constructed one (Vacuum Technology and Thin Films Research Lab, Burapha University, Thailand). The dual cathodes are a working cathode and enhancing plasma cathode as shown in Fig. 1. The titanium disc target (99.97% purity, Kurt J. Lesker) with 54 mm diameter. Argon (Ar, 99.999% purity; TIG, Thailand) and oxygen gases ( $\text{O}_2$ , 99.999% purity; TIG, Thailand) were used for sputtering and reactive gases respectively. The flow rates were separately controlled by mass flow controllers (MKS type 247D) with constant flow rates of 1.0 and 4.0 sccm. Before deposition, the chamber was evacuated to a base pressure 0.001 Pa and pre-sputtered for 5 min to clear out impure gases from the chamber and remove other foreign elements on the titanium disc surface, respectively. During deposition, the pressure, electric power, and distance of target to substrate ( $d_{\text{t/s}}$ ) were controlled at 0.5 Pa, 250W and 6cm, respectively. The deposition times were varied for 30, 60, 90, and 120 min.

### 2.2. *In vitro* testing

The samples were immersed in 30 mL of an acellular Kokubo's SBF [4] with ion concentration nearly equal to those in human blood plasma ( $\text{Na}^+$  142.0,  $\text{K}^+$  5.0,  $\text{Mg}^{2+}$  1.5,  $\text{Ca}^{2+}$  2.5,  $\text{Cl}^-$  147.8,  $\text{HCO}_3^-$  1.0, and  $\text{SO}_4^{2-}$  0.5 mM). The SBF was prepared by dissolving reagent-grade chemicals of  $\text{CaCl}_2$  (APS),  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  (Carloerba),  $\text{KCl}$  (Ajax Finechem),  $\text{NaCl}$  (Merck),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (Ajax Finechem),  $\text{NaHCO}_3$  (Ajax Fiechem), and  $\text{Na}_2\text{SO}_4$  (Ajax Fiechem) in ultra-pure water, and buffering with a pH of 7.4 using tris(hydroxymethyl)-aminomethane (APS) and 1 M HCl (J.T. Baker) at  $37^\circ\text{C}$ . Each sample was immersed at  $37^\circ\text{C}$  for 3 and 5 days. After the given immersion period, the samples were removed from the SBF, gently washed with the ultra-pure water drop by drop, and dried at room temperature.

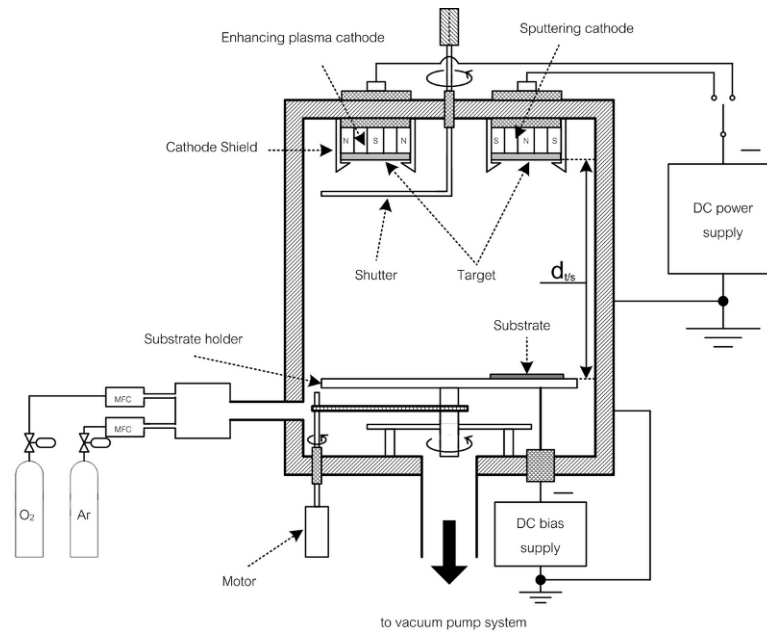


Fig. 1. Dual cathode dc unbalanced magnetron sputtering diagram.

### 2.3. Characterization

The surfaces of the films before and after immersion in SBF were analyzed using an X-ray diffractometer with a thin-film mode (TF-XRD, RINT-2100, Rigaku) adjusted with  $\text{CuK}\alpha$  radiation, 40 kV, 20 mA at a step rate of  $2\theta=2^\circ \text{ min}^{-1}$  and a  $1^\circ$  glancing angle against the incident beam. Also, the surface morphologies and composition were studied by scanning electron microscopy (SEM; LED, 1450VP). Atomic force microscopy (AFM, Veeco, Nano Scope IV) with a silicon probe was used for the observation of grain size, surface roughness, and film thicknesses with a scan size of  $1.0 \mu\text{m}^2$ .

## 3. Results and discussion

### 3.1. Deposition of Rutile $\text{TiO}_2$ Films

Figure 2 shows that the XRD patterns of  $\text{TiO}_2$  films deposited with various deposition times of 30, 60, 90 and 120 min at the  $d_{t/s}$  of 6cm. All samples were observed only (110) rutile  $\text{TiO}_2$ . Moreover, the crystallinity of (110) rutile was increased with increasing the deposition time. Shibata *et al.* [5] proposed that the (110) rutile is a result of the reaction between activated Ti or decelerated  $\text{Ti}^+$  and neutral  $\text{O}_2$  or  $\text{O}_2^-$ , moreover, anatase phase grows from the reaction between neutral Ti and neutral  $\text{O}_2$  or  $\text{O}_2^-$ . These results can be discussed in electronic effect of  $4s^2$  orbital on Ti structure. Normally, neutral Ti forms the hybridization of  $sp^3d^2$  of the third electron shell. The double electrons in 4s orbital effects on the distortion of the octahedral to form complex octahedral structure of anatase phase. In contrast, the decelerated  $\text{Ti}^+$  or activated Ti is deficient electron in 4s orbital. Therefore, rutile is formed the complete octahedral structure (the  $\theta$  between Ti and O is  $90^\circ$ ) [6]. Kasemanankul *et al.* [3] reported that the formation of rutile in dual cathode sputtering chamber due to electrons that trapped in an unbalanced magnetic field (UMF) bombarded Ti atom into  $\text{Ti}^+$ , which reacted with  $\text{O}_2$  gas and formed rutile phase. Moreover, (110) rutile can be shifted to (101) crystal plane with increasing the bias substrate voltage.

The roughness, grain size and film thickness were characterized by section analysis of AFM, which exhibits in Table 1. The roughness, grain size and thickness were increased with increasing the deposition time due to the results of mass transfer and heat accumulated on the film surface. The surface morphology of films in Fig. 3 clearly exhibited the growth of grain that is the function of deposition time.

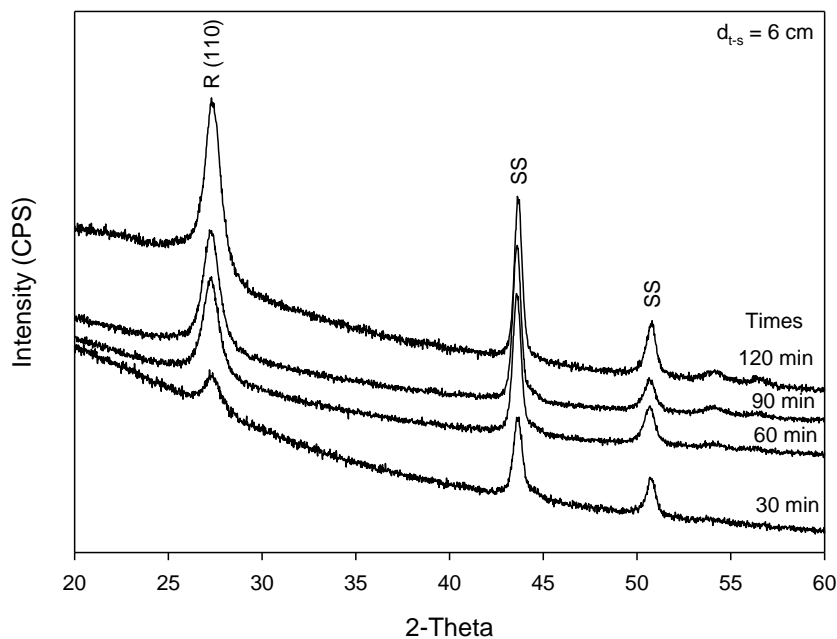


Fig. 2. XRD patterns of rutile  $\text{TiO}_2$  deposited on 316L-SS with various deposition times.

Table 1. Grain size and thickness of rutile  $\text{TiO}_2$  films deposited on 316L-SS with various deposition times.

Times	Roughness (nm)	Thickness (nm)			Mean	SD	Grain size (nm)			Mean	SD
30	1.6	106	107	106	106	0.48	74	41	47	54	17.72
60	2.6	223	219	219	220	2.24	87	75	39	67	24.94
90	2.7	323	325	324	324	0.70	97	62	81	80	17.11
120	3.0	425	427	422	425	2.22	101	37	99	79	36.09

### 3.2. Formation of apatite on the rutile $\text{TiO}_2$ films

Figure 4 shows that the XRD pattern of apatite formed on various deposition times after immersed in SBF 3 days in incubator at constant temperature of  $37^\circ\text{C}$ . The highest intensity of apatite, implying highest crystallinity, was observed on the film that deposited for 30 min. Furthermore, the moderate peak of apatite exhibited on the films that deposited for 90 min. due to the morphology of films that deposited using 30 and 90 min. shows that the homogeneous grains on the surface. Nancollas *et al.* [7, 8] investigated apatite nucleation on metal oxide in terms of surface tension and proposed that the formation of apatite on a titania gel is induced by the abundant Ti-OH groups are essential for apatite nucleation. Therefore, the apatite easy formed on the more surface area of the film.

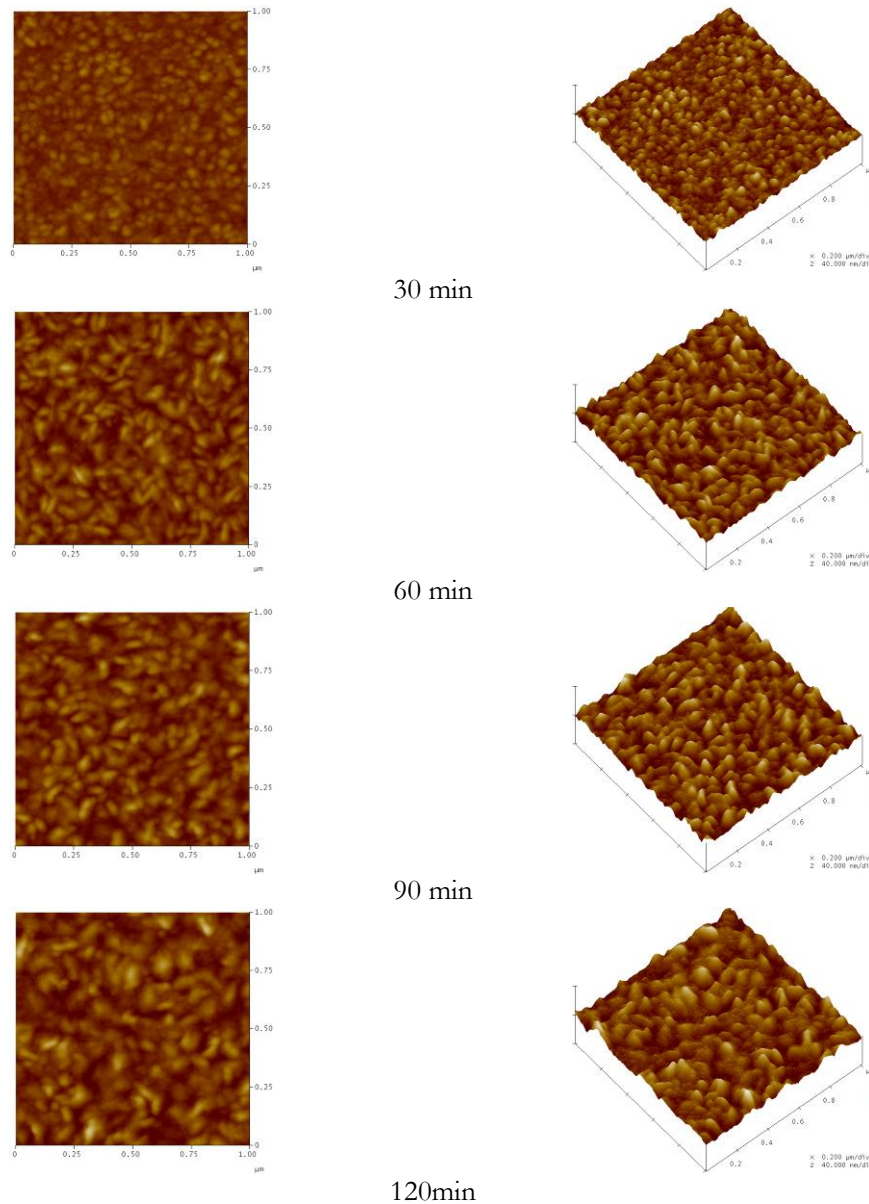


Fig. 3. 2D-, 3D AFM images of rutile  $\text{TiO}_2$  films deposited on 316L-SS with various deposition times.

The morphology of apatite with 3 days incubation time in Fig. 5 exhibits that a denser apatite layer formed on 30 min rutile film and globule like on 60 min rutile film. The dense and crack apatite layer was observed on 90 and 120 min rutile films, respectively. Moreover, high crack of apatite layer on 90 min rutile film was observed, which might increased the surface area for apatite formation in the next layer. Therefore, for incubation time increased to 5 day, which shows in Fig. 6, the crystallinity of apatite on 90 min rutile film was higher than that of on 30 min rutile film due to the apatite is a layer formation between  $\text{Ca}^{2+}$  and  $\text{PO}_4^{2-}$  in the body fluid [9]. The dense apatite layer for 3 days incubation on 30 min rutile was affected on the decrease of reaction surface area in the next layer. These results well correlated with the Nancollas *et al.* [7, 8].

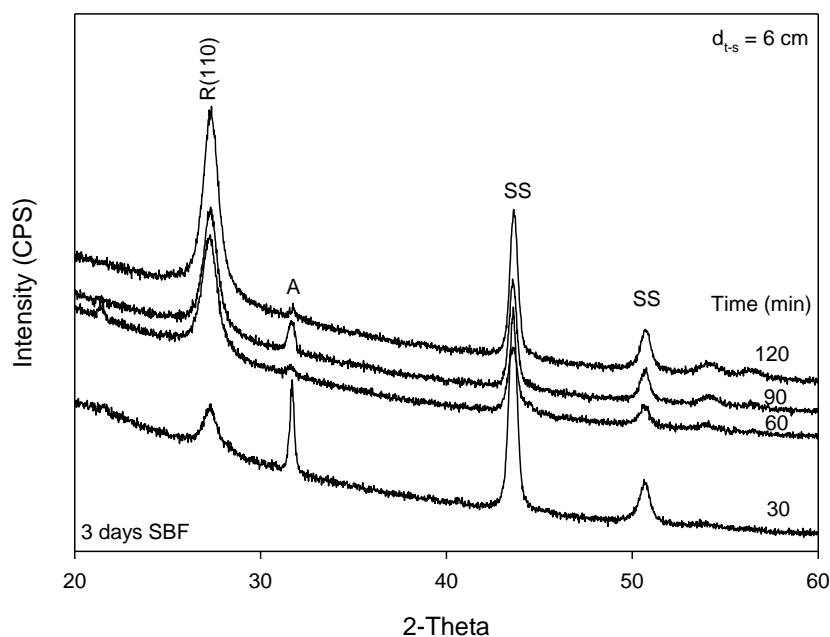


Fig. 4. XRD patterns of 3 days apatite formed on various deposition time of rutile  $\text{TiO}_2$  films (R: rutile, A: apatite).

Figure 7 shows that the SEM micrographs of the apatite formation for 5 days with various deposition times of rutile films. It was found that the globules with size of several micrometers are evidence. Each globule is actually an aggregate of numerous tiny flakes uniting together. However, the base of globule is more interested as shown in each right bottom figure. The dense globules nuclei were observed on the 90 min rutile film. In contrast, the lightly formation of globules nuclei were exhibited on the 120 min rutile film. This is because of the longer deposition of rutile film could be affected on the thermal stress inside in nature and causing the difficulty in the apatite formation.

#### 4. Conclusion

The thin rutile  $\text{TiO}_2$  films with only (110) crystal plane have been deposited by dual cathode dc unbalanced magnetron sputtering. The crystallinity of rutile was increased with increasing the deposition time due to the increasing time of mass transfer and heat diffusion to crystal arrangement. The small grain of rutile film, which deposited using 30 min, was observed excellent apatite formation in primary layer *in vitro*. However, the apatite is the layer formation of calcium and phosphate ions. Therefore, the surface area of primary layer was affected on the apatite formation in the next layer. Moreover, the higher crystallinity of apatite exhibited on the 90 min rutile film after *in vitro* for 5 days.

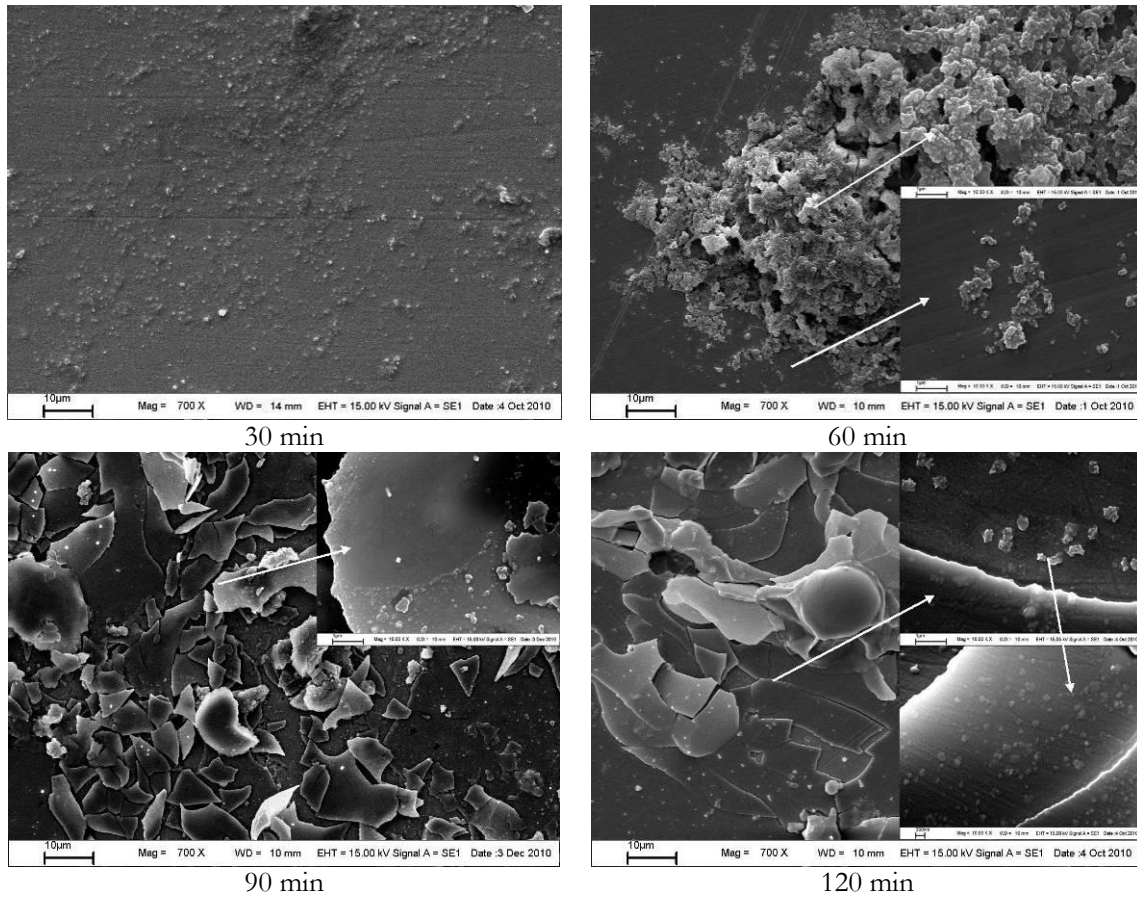


Fig. 5. SEM micrographs of 3 days apatite formed on various deposition times rutile  $\text{TiO}_2$ .

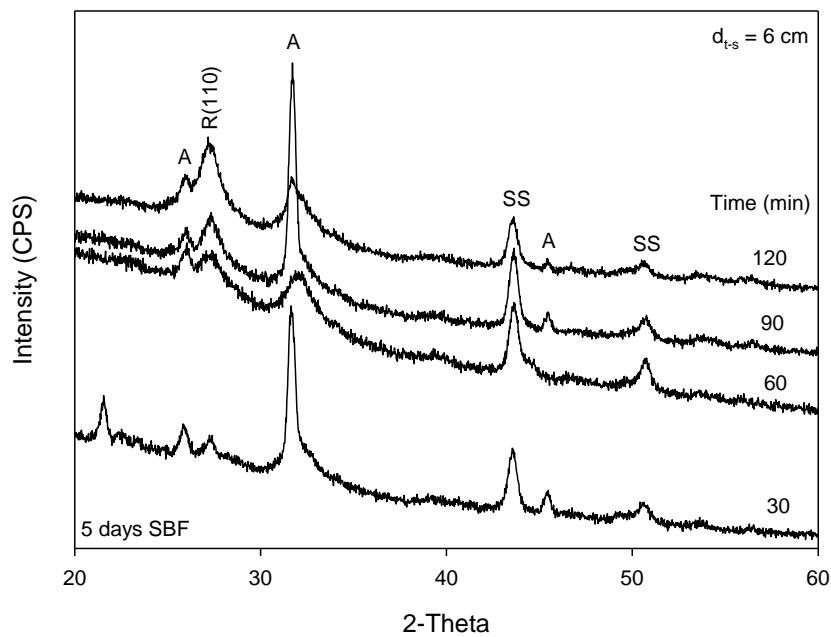


Fig. 6. XRD patterns of 5 days apatite formed on various deposition time rutile  $\text{TiO}_2$  films (R: rutile, A: apatite).

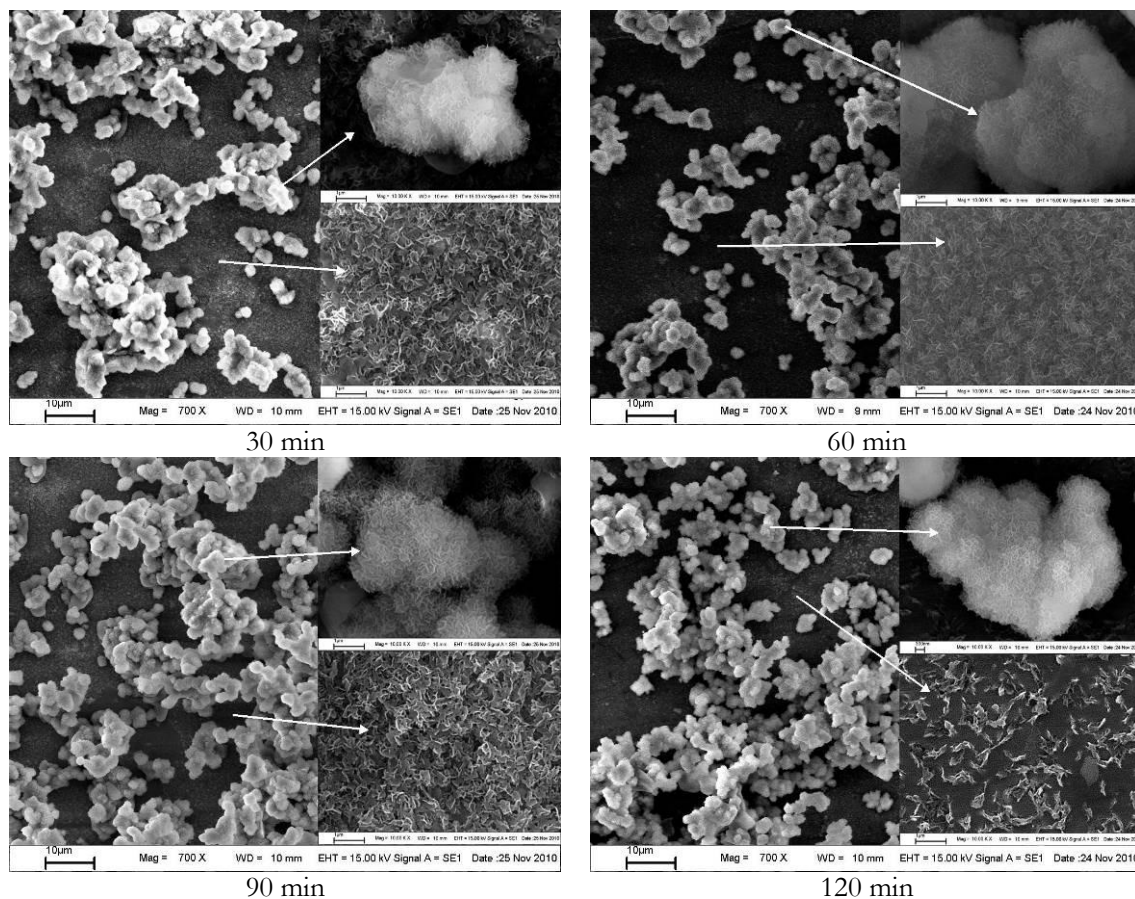


Fig. 7. SEM micrographs of 5 days apatite formed on various deposition times rutile  $\text{TiO}_2$ .

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